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(54) MAGNETIC MATERIAL FOR MICROWAVE AND HIGH FREQUENCY CIRCUIT PARTS USING THE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To make possible use so high frequency as several hundreds MHz-GHz and to bake at low temperature under 1000°C.

SOLUTION: Hexagonal crystal which includes more than a kind of alkaline earth metal elements at least as a main composition, more than one of Pb or Cu at least, Fe and O, are used as a main phase. Also hexagonal crystal ferrite which includes more than one kind of alkaline earth metal elements at least, Fe and O, is used as a main phase and includes metal oxide M_xO_y as weight% of O < M_xO_y ≤ 10 as a sub-component (M_xO_y includes more than one kind of V₂O₅, CuO, Bi₂O₃, M₀O₃, WO₂ and/or PbO).

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CLAIMS

[Claim(s)]

[Claim 1] A ceramic magnetic-substance material which makes a primary phase a hexagonal ferrite containing one or more kinds of an alkaline-earth-metal element, at least one or more kinds of lead (Pb) and copper (Cu), and iron (Fe) and oxygen (O) at least as a main presentation.

[Claim 2] A ceramic magnetic-substance material which makes a primary phase a hexagonal ferrite containing one or more kinds, and iron (Fe) and oxygen (O) of an alkaline-earth-metal element, and is characterized by what a metallic oxide M_xO_y is included for 0 < M_xO_y <= 10% of the weight as an accessory constituent (it corrects and M_xO_y is one or more kinds of V₂O₅, CuO and Bi₂O₃, and MoO₃, WO₃ and PbO(s)) at least as a main presentation.

[Claim 3] a ceramic magnetic-substance material which is characterized by providing the following and which makes a hexagonal ferrite a primary phase and is characterized by what a metallic oxide M_xO_y is included for 0 < M_xO_y <= 10% of the weight as an accessory constituent (correcting -- one or more kinds of oxides of a metal which is not contained in the main presentation among V₂O₅, CuO and Bi₂O₃, and MoO₃, WO₃ and PbO) They are one or more kinds of an alkaline-earth-metal element at least as a main presentation. At least one or more kinds of lead (Pb) and copper (Cu) Iron (Fe) and oxygen (O)

[Claim 4] A polycrystal ceramic magnetic-substance material of claim 1 - 3 term publication which contain in said main presentation further hexagonal system A₃B-2Fe₂₄O₄₁ phase (one or more kinds and B as which A was chosen from alkaline earth metal and Pb contain Co and Cu at least, including Co) at least including cobalt (Co).

[Claim 5] RF passive circuit elements characterized by having structure where a conductor was embedded into said magnetic substance, using the magnetic substance according to claim 1 to 4.

[Claim 6] RF passive circuit elements given in the 5th term of a patent claim to which a conductor in the magnetic substance is characterized by using silver (Ag) as a principal component.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention is the passive circuit elements for RFs produced using the oxide magnetic compact material and this which are used for RF passive circuit elements.

[0002]

[Description of the Prior Art] The high speed and densification of information and the communication link field progress, and high-frequency-ization of operating frequency is progressing so that commercial-scene expansion of satellite communication or mobile communications may see in recent years. As an oxide magnetic compact used by such RF, there are a nickel zinc system spinel ferrite, a garnet system ferrite, and a hexagonal ferrite. Among these, since its electrical resistivity was high, its effect of the eddy current loss loss in a RF was small, and they were usable, but since a spinel ferrite and a garnet ferrite have isotropic magnetic properties, in the RF, the natural resonance phenomenon was produced more, permeability fell with the hundreds MHz-GHz band, and they cannot be used. [of about 100MHz] On the other hand, although only a hexagonal ferrite may be able to be used to a GHz band by the magnetic anisotropy, the present condition is seldom used in fact.

[0003] Next, when producing the inductor element for RFs, and a noise filter element using these magnetic substance, for the miniaturization of an element, the structure where the conductor was embedded to the interior of the magnetic substance is desirable. That is, by taking the structure where the conductor was wound around the coiled form in the magnetic substance, the number of coiling can become large, and a magnetic-path configuration can serve as a closed magnetic circuit, and an inductance and an impedance can be enlarged. for this reason, magnetic-substance powder and a conductor -- powder is mixed with an organic binder or a solvent and it considers as the shape of a slurry, respectively, and a printing laminating is carried out by turns with a printing method of construction etc., and the small chip inductor etc. is manufactured by really calcinating this.

[0004] in this case, the conductor to be used -- as a charge of material, although it is desirable to use the silver which electrical resistivity is low and is low cost, and copper, for a ***** reason, when burning temperature is high, Pd of such conductor material etc. is expensive, and conductor material with comparatively high electrical resistivity needs to be used for them at the elevated temperature at which silver exceeds about 930 degrees C and copper exceeds about 1000 degrees C, and they is disadvantageous in respect of the element engine performance or cost. For this reason, among the various aforementioned ferrites, although the magnetic-substance ceramics which can be calcinated at low temperature is needed, since a NiZnCu spinel ferrite can be calcinated below 900 degrees C, this NiZnCu spinel ferrite is used for the laminating chip inductor.

[0005]

[Problem(s) to be Solved by the Invention] However, as mentioned above, a spinel ferrite cannot be used with the high frequency exceeding 100MHz. a hexagonal ferrite usable on the other hand more at a RF - - burning temperature -- 1200 degrees C or more -- required -- this case -- silver and copper of low cost

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low electrical resistivity -- ***** stripes -- it might be unacquainted and there was a trouble. Moreover, there was a problem also from a viewpoint of energy saving.

[0006] This invention aims at offering usable polycrystal ceramic magnetic-substance material which can be calcinated at low temperature 1000 degrees C or less and RF passive circuit elements using this to a RF called hundreds MHz-GHz in order to solve said conventional problem.

[0007]

[Means for Solving the Problem] In order to solve the above-mentioned trouble, the 1st material of this invention is one or more kinds of an alkaline-earth-metal element, at least one or more kinds of Pb and Cu, and a ceramic magnetic-substance material containing Fe and O that makes a hexagonal ferrite a primary phase at least as a main presentation. Moreover, the 2nd material of this invention is one or more kinds of an alkaline-earth-metal element, and a ceramic magnetic-substance material which makes a hexagonal ferrite containing Fe and O a primary phase, and is characterized by what a metallic oxide M_xO_y is included for 0 < M_xO_y <= 10% of the weight as an accessory constituent (it corrects and M_xO_y is one or more kinds of V₂O₅, CuO and Bi₂O₃, and MoO₃, WO₃ and PbO(s)) at least as a main presentation. In these materials, it is desirable to include it in the main presentation one or more kinds, using as an accessory constituent the metallic oxide M_xO_y which is not contained in the main presentation, including at least one or more kinds of Pb and Cu. It is desirable to include at least 24Ohexagonal system A₃B-2Fe41 phase (for one or more kinds and B as which A was chosen from alkaline earth metal and Pb to contain Co and Cu at least, including Co) including Co furthermore.

[0008] Moreover, RF passive circuit elements of this invention are RF passive circuit elements characterized by having structure where a conductor was embedded into said magnetic substance. In this element, it is desirable as a conductor in the magnetic substance to use Ag as a principal component.

[0009]

[Embodiment of the Invention] Since the material of this invention is a ceramic sintered compact, it can be manufactured in the usual ceramic production process. At this time, with the material of this invention, since Pb or Cu is replaced by the presentation, it sinters at low temperature more rather than a material conventionally. Or it sinters at low temperature rather than the conventional material too by adding V₂O₅, CuO and Bi₂O₃, and MoO₃, WO₃ and PbO. If these substitute dissolution and addition are performed to coincidence, the effect of low temperature sintering will become large further. Moreover, a RF property improves more that the main presentation is Z mold hexagonal ferrite A₃B-2Fe24O41 so-called phase (one or more kinds and B as which A was chosen from alkaline earth metal and Pb are Co, or are Co and Cu) including cobalt (Co).

[0010] If burning temperature becomes low, it is cheap, coincidence baking can be carried out, the element of the closed magnetic circuit configuration of electrode one apparatus can be built with forms which built in the electrode material of the low melting point with low electrical resistivity, such as Cu and Ag, it will be small and elements for RFs, such as a noise filter with the large impedance in the specific frequency of a RF, will be obtained by the inductor high [Q] or small.

[0011] Although Z mold (24OA3B-2Fe41 phase) containing Co is hereafter explained as a center as a representative of a hexagonal ferrite As this invention is not the object restrained by this and is shown in (an example 5) The hexagonal ferrite of other structures, i.e., M mold, (12OAF_e19 phase) When each mold of U mold (36OA4B-2Fe60 phase), W mold (16OAB2Fe27 phase), an X type (28OA2B2Fe46 phase), and Y mold (12OA2B2Fe22 phase) or these are intermingled, low-temperature baking is completely enabled similarly.

[0012] (Example 1) As a start raw material, the powder of BaCO₃, SrCO₃, PbO, CoO and CuO of 99.5% or more of purity, and alpha-Fe 2O₃ was used. After having blended so that the mole ratio of (Ba+Sr+Pb):(Co+Cu):Fe might be set to 3:2:24, the mole ratio of Ba:Sr:Pb and Co:Cu might serve as a value of (a table 1) and sum total weight might be set to 300g, mixing with the ball mill and carrying out temporary quenching of these powder at 800 degrees C for 2 hours each, the ball mill ground again. After carrying out 1 shaft pressing of this temporary-quenching powder by the pressure of 0.5 t/cm² in metal mold, it calcinated at each predetermined temperature of 50-degree-C unit with the electric furnace for 3 hours. The relative density of the obtained sample was measured and the result of having

asked for the minimum burning temperature from which 90% or more of relative density is obtained was shown in (a table 1). Moreover, the toroidal-like sample with the outer diameter of 20mm, a bore [of 12mm], and a thickness of 5mm was started from the sintered compact, and the permeability in 100MHz and 1GHz was measured. Permeability was measured on the same conditions also about the commercial NiZn system spinel ferrite for the comparison. Moreover, the sintered compact was ground and the generation phase was identified according to the X diffraction.

[0013]

[A table 1]

(°C)

Ba/Sr/Pb 量			Co置換量 (Ba, Sr, Pb) ₃ (Co _{1-x} Cu _x) ₂ Fe ₂₄ O ₄₂						
Ba	Sr	Pb	0.0	0.1	0.3	0.5	1.0	1.5	2.0
3.0	0.0	0.0	1200	1150	1050	1000	950	900	900
2.8	0.0	0.1	1150	1100	1050	1000	950	900	900
2.7	0.0	0.3	1050	1050	950	950	900	850	850
2.5	0.0	0.5	1000	1000	950	950	850	850	850
2.0	0.0	1.0	1000	1000	950	900	850	850	850
1.5	0.0	1.5	1000	1000	950	900	850	850	850
1.0	0.0	2.0	850	850	900	900	850	850	850
0.0	0.0	3.0	950	950	900	900	800	800	800
1.5	0.5	1.0	1000	1000	950	900	850	850	850
1.0	1.0	1.0	1000	1000	950	900	850	850	850
0.5	1.5	1.0	1000	1000	950	900	850	850	850
0.0	2.0	1.0	1000	1000	950	900	850	850	850

[0014] Eburnation was more possible than before at nearby low temperature by replacing alkaline earth metal by Pb, or replacing Co by Cu in the magnetic substance of this invention, so that more clearly than (a table 1). By carrying out coincidence substitute especially of Pb and Cu, baking became possible below 900 degrees C which carries out eburnation at low temperature further and which Ag does not dissolve depending on conditions. According to the X diffraction, any sample was [the hexagonal ferrite] a primary phase. Moreover, 100MHz and 1GHz of any samples of relative permeability mu' were five to about ten. Although it was 60 in the NiZn ferrite of the example of a comparison at 100MHz, it became less than five in 1GHz.

[0015] (Example 2) each powder of V₂O₅ after blending so that the mole ratio of Ba:Co:Fe may be set to 3:2:24 and sum total weight may be set to 300g by the same method as an example 1, mixing with a ball mill and carrying out temporary quenching at 800 degrees C for 2 hours each, CuO and Bi₂O₃, and MoO₃, WO₃ and PbO -- weight ***** of (a table 2) -- preferential grinding was again carried out with the ball mill. It calcinated at each predetermined temperature of 50-degree-C unit after fabricating this powder for 3 hours. The relative density of the obtained sample was measured and it asked for the minimum burning temperature from which 90% or more of relative density is obtained. The result was shown in (a table 2). Moreover, the toroidal-like sample with the outer diameter of 20mm, a bore [of 12mm], and a thickness of 5mm was started from the sintered compact, and the permeability in

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100MHz was measured. Moreover, the sintered compact was ground and the generation phase was identified according to the X diffraction.

[0016]

[A table 2]

(°C)

添加物	添加量 (wt%)							
	0	0.05	0.1	0.5	1.0	5.0	10.0	20.0
V ₂ O ₅	1200	1150	1100	1050	1000	1000	950	900
CuO	1200	1150	1100	1050	1000	1000	950	900
Bi ₂ O ₃	1200	1150	1100	1050	1000	1000	950	900
MoO ₃	1200	1150	1150	1100	1100	1050	1000	1000
WO ₃	1200	1150	1150	1100	1100	1050	1000	1000
PbO	1200	1150	1100	1050	1000	1000	950	900

[0017] Eburnation was more possible than before at nearby low temperature by adding V₂O₅, CuO and Bi₂O₃, or MoO₃, WO₃ and PbO in the magnetic substance of this invention so that more clearly than (a table 2). On the other hand, according to the X diffraction, although the hexagonal ferrite was a primary phase, the 2nd phase of any sample increased at addition 20wt%. Moreover, relative permeability became less than five at 20wt%, although addition 10wt% was five to about ten. Therefore, the maximum of an addition is 10 % of the weight.

[0018] (Example 3) After having blended so that the mole ratio of Ba:Sr:Pb:Co:Fe might be set to 1:1:1:2:24 and sum total weight might be set to 300g by the same method as an example 1, mixing with the ball mill and carrying out temporary quenching at 800 degrees C for 2 hours each, each powder of V₂O₅, CuO and Bi₂O₃, and MoO₃, WO₃ and PbO was added to the weight section of (a table 3), and preferential grinding was again carried out with the ball mill. It calcinated at each predetermined temperature of 50-degree-C unit after fabricating this powder for 3 hours. The relative density of the obtained sample was measured and the result of having asked for the minimum burning temperature from which 90% or more of relative density is obtained was shown in (a table 3). Moreover, the toroidal-like sample with the outer diameter of 20mm, a bore [of 12mm], and a thickness of 5mm was started from the sintered compact, and the permeability in 100MHz was measured. Moreover, the sintered compact was ground and the generation phase was identified according to the X diffraction.

[0019]

[A table 3]

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(°C)

添加物	添加量 (wt%)							
	0	0.05	0.1	0.5	1.0	5.0	10.0	20.0
V ₂ O ₅	1000	950	900	900	900	850	850	800
CuO	1000	950	900	900	900	850	850	800
Bi ₂ O ₃	1000	950	900	900	900	900	850	850
MoO ₃	1000	1000	950	950	900	900	900	850
WO ₃	1000	1000	950	950	900	900	900	850
PbO	1000	1000	1000	1000	950	950	950	900

[0020] clearer than (a table 3) -- as -- the magnetic substance of this invention -- V₂O₅, and CuO and Bi₂ -- by adding O₃ or MoO₃, eburnation is more possible than before at nearby low temperature, and baking at 900 degrees C or less which Ag does not dissolve depending on conditions was attained. On the other hand, an effect with remarkable addition of PbO was not accepted. This is considered because PbO is already included as a primary phase. On the other hand, according to the X diffraction, although the hexagonal ferrite was a primary phase, the 2nd phase of any sample increased at addition 20wt%. Moreover, relative permeability became less than five at 20wt%, although addition 10wt% was five to about ten. Therefore, the maximum of an addition is 10 % of the weight.

[0021] (Example 4) After having blended so that the mole ratio of Ba:Sr:Co:Cu:Fe might be set to 1.5:1.5:1:1:24 and sum total weight might be set to 300g by the same method as an example 1, mixing with the ball mill and carrying out temporary quenching at 800 degrees C for 2 hours each, each powder of V₂O₅, CuO and Bi₂O₃, and MoO₃, WO₃ and PbO was added to the weight section of (a table 4), and preferential grinding was again carried out with the ball mill. It calcinated at each predetermined temperature of 50-degree-C unit after fabricating this powder for 3 hours. The relative density of the obtained sample was measured and the result of having asked for the minimum burning temperature from which 90% or more of relative density is obtained was shown in (a table 4). Moreover, the toroidal-like sample with the outer diameter of 20mm, a bore [of 12mm], and a thickness of 5mm was started from the sintered compact, and the permeability in 100MHz was measured. Moreover, the sintered compact was ground and the generation phase was identified according to the X diffraction.

[0022]

[A table 4]

(°C)

添加物	添加量 (wt%)							
	0	0.05	0.1	0.5	1.0	5.0	10.0	20.0
V ₂ O ₅	1000	950	900	900	900	850	850	800
CuO	1000	1000	1000	1000	1000	1000	1000	950
Bi ₂ O ₃	1000	950	900	900	900	850	850	800
MoO ₃	1000	1000	950	950	950	900	900	900
WO ₃	1000	1000	950	950	950	900	900	900
PbO	1000	950	900	900	900	900	850	800

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[0023] In the magnetic substance of this invention, by adding V₂O₅, Bi₂O₃, or MoO₃ and PbO, eburnation is more possible than before at nearby low temperature, and baking at 900 degrees C or less which Ag does not dissolve depending on conditions was attained so that more clearly than (a table 4). On the other hand, an effect with remarkable addition of CuO was not accepted. This is considered because CuO is already included as a primary phase. On the other hand, according to the X diffraction, although the hexagonal ferrite was a primary phase, the 2nd phase of any sample increased at addition 20wt%. Moreover, relative permeability became less than five at 20wt%, although addition 10wt% was five to about ten. Therefore, the maximum of an addition is 10 % of the weight.

[0024] By the same method as an example 1, the mole ratio of Ba:Pb:Fe serves as a ratio of (a table 5). (Example 5) each powder of V₂O₅ after blending so that sum total weight may be set to 300g, mixing with a ball mill and carrying out temporary quenching at 700 degrees C for 2 hours each, CuO and Bi₂O₃, and MoO₃, WO₃ and PbO -- 1.0wt(s)% -- with what was added What is not added was built and preferential grinding was again carried out with the ball mill, respectively. These powder was fabricated and it calcinated at each predetermined temperature of 50-degree-C unit for 3 hours. The relative density of the obtained sample was measured and it asked for the minimum burning temperature from which 90% or more of relative density is obtained. Moreover, the sintered compact was ground and the generation phase was identified according to the X diffraction. The result was shown in (a table 5).

[0025]

[A table 5]

(°C)

試 料 No	主組成 (mol比)					副成分 (1 wt%)						主 要 相
	Ba	Pb	Co	Cu	Fe	--- V ₂ O ₅ CuO Bi ₂ O ₃ MoO ₃ WO ₃ PbO						
1	1	0	0	0	12	1300	1150	1100	1150	1200	1200	M
2	0.7	0.3	0	0	12	1100	950	900	1000	1050	1050	M
3	2	0	2	0	12	1200	1050	1050	1050	1100	1100	Y
4	1.5	0.5	2	0	12	1050	950	950	1000	1000	1000	Y
5	2	0	1.5	0.5	12	1000	800	1000	900	950	950	Y
6	1.5	0.5	1.5	0.5	12	900	850	900	850	850	850	Y
7	1	0	2	0	16	1200	1050	1050	1050	1100	1100	W
8	0.7	0.3	2	0	16	1050	950	950	950	1000	1000	W
9	1	0	1.5	0.5	16	1000	900	1000	900	950	950	W
10	0.7	0.3	1.5	0.5	16	900	850	900	850	850	850	W
11	2	0	2	0	28	1250	1050	1050	1050	1150	1150	X
12	1.5	0.5	2	0	28	1100	950	950	1000	1000	1050	X
13	2	0	1.5	0.5	28	1000	900	1000	900	950	950	X
14	1.5	0.5	1.5	0.5	28	900	850	900	850	850	850	X
15	4	0	2	0	36	1250	1050	1050	1050	1150	1150	U
16	3	1	2	0	36	1100	950	950	950	1050	1050	U
17	4	0	1.5	0.5	36	1000	900	1000	900	950	950	U
18	3	1	1.5	0.5	36	900	850	900	850	850	850	U

[0026] Eburnation was more possible than before at nearby low temperature by replacing PbO or CuO or adding V₂O₅, CuO and Bi₂O₃, or MoO₃ and PbO so that more clearly than (a table 5). Moreover, by performing these to coincidence, sintering at 900 degrees C or less also became possible. According to the X diffraction, any sample was [the hexagonal ferrite] a primary phase.

[0027] (Example 6) 20V after blending so that mole ratio of Ba:Sr:Co:Cu:Fe may be set to 1.5:1.5:1.5:0.5:24 and sum total weight may be set to 300g by the same method as example 1, mixing with ball mill and carrying out temporary quenching at 850 degrees C for 2 hours each5 powder -- 1.0wt

(s)% -- in addition, preferential grinding was again carried out with the ball mill. This powder was fabricated in the outer diameter of 3mm, and bore of 1mm, and it calcinated at 900 degrees C for 3 hours. It was about 10 when the relative permeability of the obtained sintered compact was measured by 1MHz. The conductor was used as through and a bead mold noise filter in the hole of the center of this sample. The noise filter of the same configuration was produced using the NiZn system spinel ferrite of marketing of various permeability for the comparison. The impedance in 1GHz was measured about these filters. The result was shown in (a table 6).

[0028]

[A table 6]

No.	材料系	比透磁率 (1MHz)	インピーダンス (Ω at 1GHz) 実部X 虚部R Z			実/比
1	六方晶	1.0	5.8	1.8	6.1	実施例
2	NiZn系	1.00	~0	4.1	4.1	比較例
3	NiZn系	2.5	~0	4.8	4.8	比較例
4	NiZn系	1.0	1.1	2.6	2.8	比較例

[0029] The direction of the material of this invention has a large impedance Z, and is superior to the NiZn system spinel ferrite as a charge of a noise absorber so that more clearly than (a table 6).

[0030] Moreover, when it thinks as an inductance element, by the NiZn system, in every sample, the real part (namely, real part of permeability) of an impedance falls, and has become below imaginary part by 1GHz. As an inductor, since, as for operating threshold frequency, Q value is considered to be one or more, i.e., frequency with the larger real part of permeability than imaginary part, it is clear that operating threshold frequency's as an inductor of this NiZn system material it is 1GHz or less. On the other hand, with the material of this invention, real part X is larger than imaginary part R, the real part of permeability does not fall in 1GHz in 1GHz, but Q value is larger than 1. Therefore, it is usable to a RF rather than it exceeds 1GHz.

[0031] (Example 7) 2OBiafter blending so that mole ratio of Ba:Sr:Co:Cu:Fe may be set to 2:1:1.5:0.5:24 and sum total weight may be set to 300g by the same method as example 1, mixing with ball mill and carrying out temporary quenching at 900 degrees C for 2 hours3 powder -- 1.5wt(s)% -- in addition, preferential grinding was again carried out with the ball mill. The organic binder was mixed to this temporary-quenching powder, and the uniform green sheet was formed with the doctor blade method. The green sheet produced using NiZnCu system spinel ferrite powder for the comparison was also prepared. On the other hand, the **** paste which comes to mix BIBIKURU was prepared for Ag, and it printed on the previous green sheet at the coiled form. The green sheet of one more sheet was applied on it, the pressure was applied in the thickness direction in piles, it was stuck by pressure and the green sheet layered product by which the electrode was sandwiched by the magnetic substance was produced. 3hr baking of this was carried out at 910 degrees C. Ag paste was applied to the location of the inner conductor of the side of the obtained sintered compact, and by the ability being burned for 10 minutes at 700 degrees C, the external electrode was formed and it considered as the inductance element. When L value of the obtained inductor was measured by 1GHz, by the thing of this invention, it is improved 30% or more with about 20 nH(s) to having been about 15 nH(s) in the thing using a NiCuZn system spinel ferrite.

[0032]

[Effect of the Invention] This invention is the hexagonal ferrite sintered compact for RFs which can be calcinated at low temperature as explained above. Moreover, they are the RF passive circuit elements using this. it is like [by this invention, manufacture of the ferrite for RFs is attained easily, and / since it can calcinate below 900 degrees C] Ag or Cu -- cheap -- low -- an electrode material [****] -- or dielectric materials etc. and coincidence baking are possible and high performance and small RF passive circuit elements are obtained more.

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